

Role of Diffusion in Two-dimensional Bimolecular Recombination

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Experiments on carrier recombination in two-dimensional organic structures are often interpreted in the frame of the Langevin model with taking into account only the drift of the charge carriers in their mutual electric field. While this approach is well justified for three-dimensional systems, it is in general not valid for two-dimensional structures, where the contribution of diffusion can play a dominant role. We study the two-dimensional Langevin recombination theoretically and find the critical concentration below which diffusion cannot be neglected. For typical experimental conditions, neglecting the diffusion leads to an underestimation of the recombination rate by several times.

The problem of charge carrier recombination is one of the central problems in the solid state physics since recombination processes determine all optoelectronic properties of a device or a material under study. For instance, recombination can be an important factor limiting the conversion efficiency in organic solar cells. In low-mobility organic semiconductors charge carrier recombination is usually dominated by the Langevin bimolecular mode.¹ Langevin recombination is characterized by the rate limiting step being *finding* the opposite charge carrier, independent of the subsequent recombination mechanism. It is well-known that in the three-dimensional (3D) case the Langevin recombination rate is determined by drift motion of charge carriers due to their mutual Coulomb attraction and that diffusion can be neglected.² The recombination rate per unit volume equals $(\mu_e + \mu_h)eN_e^2/(\varepsilon\varepsilon_0)$, where N_e is the electron density which is assumed to be equal to the hole density $N_e = N_h \equiv N$, μ_e and μ_h are the electron and hole mobilities, respectively, $\varepsilon\varepsilon_0$ is the dielectric permittivity, and e is the electronic charge.²⁻⁴ This result is obtained by integrating the drift flux of electrons through a spherical surface of radius r surrounding a hole. Since the electric field scales as r^{-2} and the surface area of the sphere scales as r^2 , the value of r chosen is unimportant, leading to a simple solution with constant electron density, thus justifying the neglect of diffusion.² The recombination rate per unit volume is often written in the form βN^2 via the bimolecular recombination coefficient $\beta = e(\mu_e + \mu_h)/\varepsilon\varepsilon_0$, independent of carrier concentration in 3D.

Numerous recent experimental studies on bulk heterojunction solar cells have demonstrated that the recombination in organic materials with lamellar structures is much slower than what is predicted by Langevin's theory.⁵⁻¹⁴ Hence, in these films, where 2D conductivity mode is expected, the bimolecular recombination coefficient depends on the charge carrier density N .^{3,4,11-13} The straightforward reformulation of the Langevin 3D formalism for the 2D case indeed gives a concentration-

dependent recombination coefficient $\beta_{2D} \propto N^{1/2}$ if only the drift motion is taken into account. This result was considered as an explanation of the experimental data.^{3,4}

It is easy to understand the latter result rewriting the recombination rate per unit volume in the form $\mathcal{R}_{rec} = N/t$, where t is the so-called recombination time. Remarkably in any model that neglects diffusion, the recombination time in 2D is proportional to $N^{-3/2}$, and consequently the recombination rate per unit volume is proportional to $N^{5/2}$. It follows from the fact that there is only one combination of the parameters $\varepsilon_0\varepsilon$, e , μ and N (not related to diffusion), which has the dimensionality of time: $(\varepsilon_0\varepsilon/e\mu)N^{-3/2}$.

It is however not possible to neglect the contribution of diffusion to the bimolecular Langevin recombination in 2D systems.² In two dimensions, the electric field still scales as r^{-2} , but the integration takes place over a circle of circumference $2\pi r$. To achieve a recombination current which is independent on r requires a density of electrons which varies with r . The presence of a carrier density gradient means that diffusion must be explicitly included in the problem.²

The combined effects of the drift and diffusion on the bimolecular recombination in 2D has been studied by Greenham and Bobbert.² In the following we first briefly repeat their arguments. Afterwards we solve the obtained equations analytically and compare the results with Ref. 2. Finally we reformulate the model of Ref. 2 in order to make it compatible with the model considered in Refs. 3,4 in order to estimate the effect of diffusion. It will be shown that the effect depends essentially on the total concentration of charge carriers.

The following model was considered by Greenham and Bobbert.² Electrons come uniformly to a circular area around a hole. The radius R of the circle is chosen so that its inverse area is equal to the hole concentration N_h :

$$(\pi R^2)^{-1} = N_h. \quad (1)$$

The hole at the origin serves as a drain for incoming

electrons. Electrons can move within this area, due to drift in the electric field of the hole,

$$\mathbf{E}(\mathbf{r}) = \frac{e}{4\pi\epsilon_0\epsilon} \frac{\mathbf{r}}{r^3}, \quad (2)$$

and also due to diffusion.

This model can be formalized via the following set of equations for the electron flux density $\mathbf{J}(\mathbf{r})$ and the coordinate-dependent electron concentration $n(\mathbf{r})$:

$$\begin{aligned} \nabla \cdot \mathbf{J}(\mathbf{r}) &= f, \\ \mathbf{J}(\mathbf{r}) &= -\mu n(\mathbf{r}) \mathbf{E}(\mathbf{r}) - D \nabla n(\mathbf{r}), \end{aligned} \quad (3)$$

that is fulfilled in the range $0 < r < R$. Here D is the diffusion coefficient ($D = \mu kT/e$ according to Einstein's relation), f is the incoming flux of electrons. The boundary conditions for this problem are the following: $J(R) = 0$ (there is no electron flux out of the circular area), and $n(0) = 0$ (the hole is an ideal absorber of electrons). Solving this set of equations, one can obtain the recombination time t as

$$t = \langle n(\mathbf{r}) \rangle / f, \quad (5)$$

where $\langle n(\mathbf{r}) \rangle$ denotes the concentration averaged over the circular area. Then one can obtain the recombination rate \mathcal{R}_{rec} as

$$\mathcal{R}_{rec} = N_e / t, \quad (6)$$

where N_e is the total electron concentration in the system.

The result of Greenham and Bobbert² can be conveniently represented in terms of the dimensionless parameters

$$\tilde{R} = \frac{R}{a}, \quad \tilde{t} = t \frac{D}{a^2}, \quad (7)$$

where $a = e^2 / 4\pi\epsilon_0\epsilon kT$ is the Onsager radius:

$$\tilde{t} = \left(\tilde{R}^2 - \frac{1}{2} \right) G_{23}^{31} \left(\frac{1}{\tilde{R}} \left| \begin{array}{c} 0, 3 \\ 0, 0, 2 \end{array} \right. \right) + \frac{\tilde{R}}{6} - \frac{\tilde{R}^2}{8}, \quad (8)$$

where G is the Meijer G function. From equations (1), (6), (7), and (8) one can obtain the concentration dependence of the recombination time.

Greenham and Bobbert² analyzed the obtained result numerically and suggested for the concentration dependence of the recombination time a power-law interpolation: $t \sim N_h^{-1.43}$. (As mentioned above, we will assume that electron and hole concentrations are equal: $N_e = N_h \equiv N$.) Using Eq. (6) one obtains then the following dependence for the recombination rate: $\mathcal{R}_{rec} \sim N^{2.43}$.

One should however mention that the above interpretation of the numerical result is valid only in a restricted range of concentrations. In order to obtain a more general picture, let us consider the limiting cases of large

and small concentrations. For this purpose let us use the following series expansions of the Meijer G function:

$$G_{23}^{31} \left(\frac{1}{x} \left| \begin{array}{c} 0, 3 \\ 0, 0, 2 \end{array} \right. \right) = \frac{x}{3} - \frac{x^2}{4} + \frac{2x^3}{5} + O(x^4) \text{ at } x \rightarrow 0, \quad (9)$$

$$G_{23}^{31} \left(\frac{1}{x} \left| \begin{array}{c} 0, 3 \\ 0, 0, 2 \end{array} \right. \right) = \frac{\log x}{2} - \frac{2\gamma + 1}{4} + o(1) \text{ at } x \rightarrow \infty. \quad (10)$$

Here $\gamma \approx 0.577$ is Euler's constant.

Let us first consider the limit of large concentrations, i. e. small \tilde{R} . Taking into account the expansion (9), it is easy to show that

$$\tilde{t} = \frac{2}{15} \tilde{R}^3 + O(\tilde{R}^4), \quad (11)$$

whence the dependence $t(N)$ follows the relation:

$$t = \frac{2}{15\pi^{3/2}aD} N^{-3/2} \equiv \frac{8}{15\sqrt{\pi}} \frac{\epsilon_0\epsilon}{e\mu} N^{-3/2}. \quad (12)$$

Consequently, $\mathcal{R}_{rec} \sim N^{2.5}$, in accordance to the result of Juška *et al.*,³ where only drift was taken into account and diffusion was neglected. Remarkably, *in the case of high carrier concentrations N the contribution of diffusion to the recombination rate is not important.* Notably our coefficient of proportionality ($15\sqrt{\pi}e\mu/8\epsilon_0\epsilon$) appears 2.5 times larger than the one given in Ref. 3. This difference comes from different assumptions in the models: in Ref. 3 each electron was considered to start at the same distance R from the hole, while in the model considered above (Ref. 2), the starting points of electrons were chosen randomly within the circle of radius R .

We reformulate the formalism of Greenham and Bobbert² adjusting it to the model assumptions of Juška *et al.*^{3,4} To do so one has to replace the uniform influx of electrons inside the circular area by the influx from only the periphery of the circle. Then Eq. (3) takes the form:

$$\nabla \cdot \mathbf{J}(\mathbf{r}) = 0, \quad (13)$$

with replacing the boundary condition $J(R) = 0$ by the relation $J_z(R) = -fR/2$. This condition provides the same average influx of electrons as Eq. (3). The solution of this modified problem gives instead of Eq. (8) the following expression:

$$\tilde{t} = \tilde{R}^2 G_{23}^{31} \left(\frac{1}{\tilde{R}} \left| \begin{array}{c} 0, 3 \\ 0, 0, 2 \end{array} \right. \right). \quad (14)$$

In the limit of small \tilde{R} (i. e. high concentrations) one can keep only the first term of the expansion (9) and obtain:

$$\tilde{t} = \frac{1}{3} \tilde{R}^3 + O(\tilde{R}^4), \quad (15)$$

and consequently

$$t = \frac{4}{3\sqrt{\pi}} \frac{\epsilon_0\epsilon}{e\mu} N^{-3/2}, \quad (16)$$

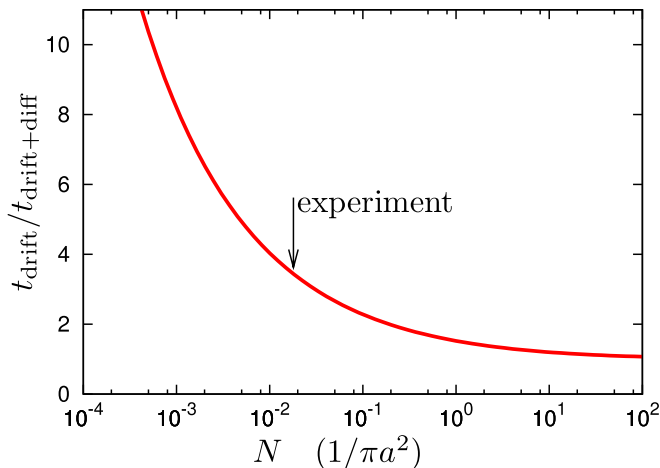


FIG. 1: The ratio between the recombination times t_{drift} obtained by taking only drift into account [Eq.(16)] and $t_{\text{drift+diff}}$ obtained when considering both drift and diffusion [Eq.(14)], as a function of the charge carrier concentration N . The concentration is measured in units of the number of charge carriers inside the Onsager radius a . The arrow corresponds to the experimental concentration in Ref. 3.

which is exactly the result of Juška *et al.*^{3,4} Figure 1 illustrates that at high carrier concentrations one can indeed neglect the contribution of diffusion to the recombination time. However, the smaller is the concentration the more important is the contribution of the diffusion process. For instance, at carrier concentrations in the experiments reported in Ref. 3 neglecting the contribution of diffusion gives a recombination time three times longer than when diffusion is included. At lower concentrations this overestimation can reach orders of magnitude. Fig. 1 shows that within the accuracy of 50 % the neglect of diffusion is justified for concentrations $N \gtrsim N_c = \frac{1}{\pi a^2}$. In other

words, if the average distance between an electron and a hole is larger than the Onsager radius a , which is the case at low charge carrier concentrations, one cannot neglect the contribution of diffusion to the Langevin recombination in 2D systems.

Let us therefore pay more attention to the limit of low concentrations. Using equations (1), (7), (8), (10), and (14) one comes to the conclusion that in this case the concentration dependence of the recombination time has the form:

$$t = \frac{1}{4\pi D} N^{-1} \log \frac{\alpha}{a^2 N}, \quad (17)$$

where the numeric constant α is $1/(\pi e^{2\gamma+3/2}) \approx 0.022$ for uniform generation of carriers inside the circular area, as considered in Ref. 2, and $1/(\pi e^{2\gamma+1}) \approx 0.037$ for generation of carriers on the periphery of the circle, as considered in Refs. 3,4. In the limit $N \rightarrow 0$, the recombination rate reads

$$\mathcal{R}_{rec} = \frac{N}{t} = 4\pi D N^2 \left(\log \frac{\alpha}{a^2 N} \right)^{-1}. \quad (18)$$

Using for the recombination rate per unit volume the traditional notation βN^2 we conclude that in the limit of low concentrations N , the bimolecular recombination coefficient β depends logarithmically on N . This dependency is essentially weaker than the one predicted by considering solely the drift processes.^{3,4}

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